Environment Engineering: Chemical Processes
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Module No # 05
Lecture No # 22
Carbonate System: Closed System

So hello everyone welcome back so we have been discussing our acid and base systems in previous lecture session right. And we have been deriving in greater detail with respect to the application and the application anyway we have been looking at was given initial concentration of various acids or bases what would be the equilibrium concentration and obviously what would be PH at equilibrium.

Right this is what we been looking into and we looked into them in greater detail and then we moved on to log CPH graphs right and as we discussed the log CPH diagram will give us idea about how the system changes with PH right. And again there were widely used in the past and I guess still widely used in India as of now. But with you particular knowledge or background you are gaining with respect to the able to use VMINTEQ right and also with respect to the mathematical tools available such as excel and such you can do away with what is now log CPH diagrams.

But again still whenever you are looking for snap shot of the system and if you have one ready available I am talking about log CPH graph here you have always have a look at it right. So again now we are going to move further and we are going to look at particular acid base system pardon me which we come across everywhere in natural system send in the engineering system right.

And obviously this is (()) (01:51) right or omni present what does it mean at something that present everywhere and considerable concentration right and if you have not guessed it already we going to be carbonate system and why carbonate physically because sub surface you have pulse of carbonate and in the atmosphere you have carbon dioxide so both of these more or less will effect your carbonate system and thus because both these deposits and carbon dioxide in atmosphere are present that is almost always going to lead to considerable concentration of your carbonate system or the carbonic acid or the Bi carbonate or CO32- right.

So we are going to look at this system in greater detail about the next two lecture sessions at least I believe so let us move on to what we are going to look at here.

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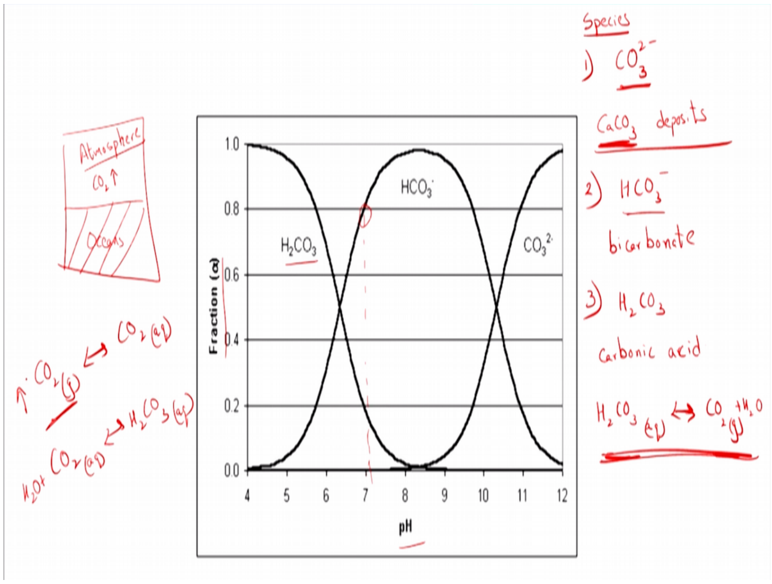

So what are some of the species we are going to look at here right here is the graph that we are going to look at so we will come back to this so the species primarily or CO32- the carbonate so we are going to identify the species in this acid base system so there are major species that we are concerned with that are going to be at equilibrium in your aqueous phase.

The first one is the carbonate the other is bi carbonate and last one is carbonic acid and the carbonic acid is obviously go into straight equilibrium with carbon dioxide in your gaseous phase so let us go by 1 by 1 so CO32- importance source of this is your CSO3 deposits right and this is the subsurface or you know ocean in such or ocean in the bed and so on. So in general we have considerable source of CACO3 and the second case is going to the second case of that we are going to look at is bicarbonate.

And as you see from this particular log pardon me the speciation diagram here right at PH7 right and where is PH7 you see that bicarbonate is the predominant form of the species that is going to be present right and the predominate species in the carbonate system so again at natural PH or natural PH pardon me the bicarbonate is the particular around that you are always concerned with and the is what we see here again let us move on to the last particular species that is H_2CO_3 the carbonic acid pardon me.

So this carbonic acid which is going to be in the aqueous phase is going to be in equilibrium with carbon dioxide in the gaseous phase right H_2O H_2CO_3 H balance so what is this mean now let us say right let us I have the beaker of water let us I have put it up or leave it open to the atmosphere right what is going to happen now. We have carbon dioxide in the gaseous phase or in the atmosphere around it.

So over some time let us say or few days or a day depending upon the temperature and the condition in that particular room right you are going to have an equilibrium between the carbon dioxide in the atmosphere or the gaseous phase and the carbonic acid in the aqueous phase riht this is the equilibrium phase equilibrium here again right. So that is going to achieve over time and that is the equation that we are going to look at H_2CO_3 here right.

And this is one particular aspect I want to stress upon so people might have earned of global warming right and you talk about this green house is gases carbon dioxide methane and so on but one aspect that maybe that has not received as much attention but the scientific community is quickly aware of it is that increase in carbon dioxide concentrations. So think of this now other than the global warning potential once major aspect that threatens the way of life in our aquatic systems is going to be the PH or the change in PH or the drop in PH so think of this now.

So you have your atmosphere let us say I am going to model this with earth and these and are your oceans right. So as the carbon oxide concentration in your gaseous phase keeps increasing right so that is what we are looking at so obviously there is going to be equilibrium with the carbon dioxide in the gaseous phase with the carbon dioxide that is going to be dissolved in your aqueous phase and obviously as we just looked at it you know carbon di oxide aqueous phase is going to stay as H_2CO_3 as carbonic acid.

So what is this mean now so as you keep increasing the concentration of your or the partial pressure of your carbon dioxide right what is going to happen now for going to increase the concentration of H_2CO_3 in your ocean H_2CO_3 you know right with our background in the past few classes is an acid that can donate a proton depending on the PH right so what is going to happen here you are going to decrease the or have a slight decrease anyway because we are going to look at large volumes here and the PKA 2 is relatively high.

So anyway there is going to decrease if you have slight decrease or there has been a decrease of the PH of the oceans now and the key issue here is that most of the aquatic system are almost all the aquatic systems are remarkably sensitive to PH or any change in PH. So as the PH drops let us say even by point 1 let us say you know I think 6.7 into 6.5 or so.

Let us look at the graph in next lecture session or one after than so if you look at let us say the PH as dropped or increase in carbon dioxide concentration have an effect on the PH of your oceans now and that has remarkable effect or you know cascading effect on your particular aquatic systems or acetic life.

So that is something that we need to be again accurately aware of other the just the global warming potential right.

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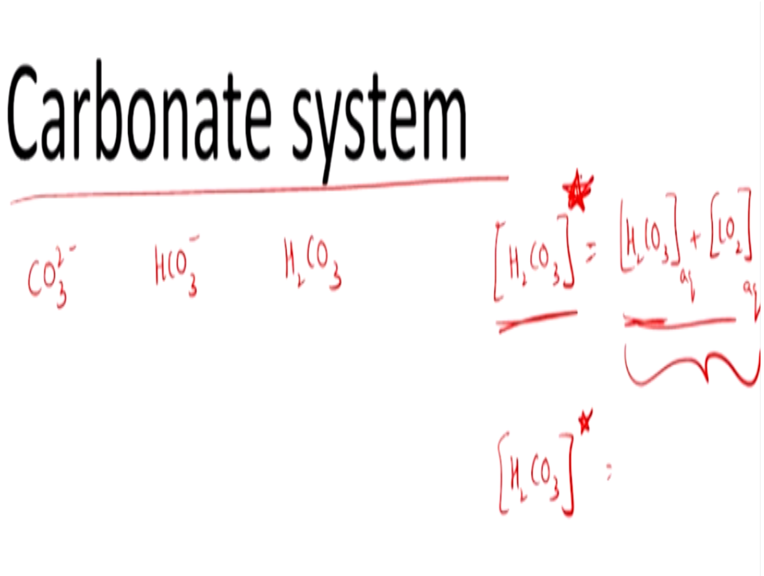

Carbonate system

CO_3^{2-} HCO_3^- H_2CO_3

$[H_2CO_3]^* = [H_2CO_3]_{aq} + [CO_2]_{aq}$

$[H_2CO_3]^* :$

So again let us come back to our particular cases here so we are talking about the carbonate and why is ubicutas does not everywhere and three species that we in general look at are CO32- with bi carbonate and the carbonic acid and as we just talked about the carbonic acid right can stay in the form of H2CO3 itself and the aqueous phase or as dissolved carbon dioxide right dissolved carbon dioxide.

So in general we people talk about carbonic acid they refer to both dissolved carbon dioxide and the actual carbonic acid in the water. So again some people use the notation with respect to (()) (09:16) let us say right and on the referring to so whenever you see H2CO3 with the (()) (09:23) this is what it mean to right different what do we say terms more or less or terminology. So now we ar going to dig into it so again if you go further you know this is an acid base system right.

So obviously what are the major aspect you need to think of right it is going to be the PKA hat does the PKA of the system and as you it is a diprotic acid it is H2CO3 so it can give out 2 protons depending on the PH so we are also going to look at the PH of the system and we are going to look at the 2 acid disassociation constants right.

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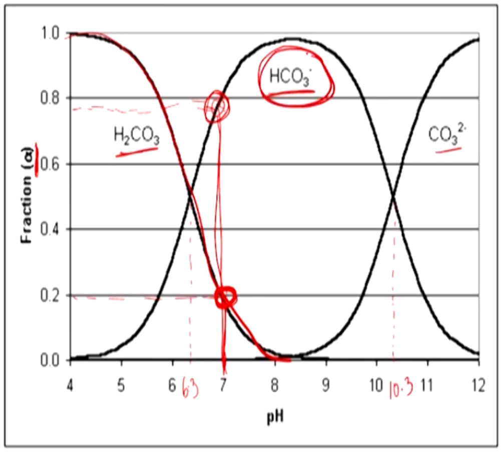
$$A_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$



$$\alpha_0 = \frac{[H_2CO_3]}{A_t}$$

$$\alpha_1 = \frac{[HCO_3^-]}{A_t}$$

$$\alpha_2 = \frac{[CO_3^{2-}]}{A_t}$$

So as we see from this particular graph here it is going to be around 6.3 and 10.3 right. But we are in general concerned the neutral PH so as we see at neutral PH most of it almost 80% of it as you see this is the ionization fraction and what does this ionization fraction give an idea about let us write them down or alpha naught, alpha1 and alpha 2 that is going to be equal to H2CO3 the concentration by the total acid or let me just try total acid here and we are going to define total acid like we did elsewhere as some all the conjugate acid and base species right.

And alpha 1 will give an idea about the fraction that is present as HCO3 or bicarbonate I guess HCO3 – and alpha to is going to be an idea about the carbonate fraction as carbonate right and alpha naught alpha 1 and alpha 2 that is what we see here so you know coming back to graph again at PH7 we have almost 80% of it as HCO3 – and some of it as 20% as OH2CO3 right this is your H2CO3 graph and that is what you see here.

So the 2 species of the carbonate system that obviously are present at you neutral species PH are going to HCO3 – and H2CO3 and obviously as you see from this particular graph with respect to the speciation you see that PKA 2 is 10.3 so thus the CO32- only going to be present in the system at the relatively higher PH right and that is the take home message here.

So in general again we are concerned with HCO3- and H2CO3 and mostly with HCO3- right and this particular bicarbonate ion or anion is going to affect your system in multiple ways their applications are which we are going to look at further down the line let us see right. So obviously again we are now going to look at particular system with respect to predicting the equilibrium values right of the various species right equilibrium concentration pardon of the various species give and that you have initial concentration of some relevant components.

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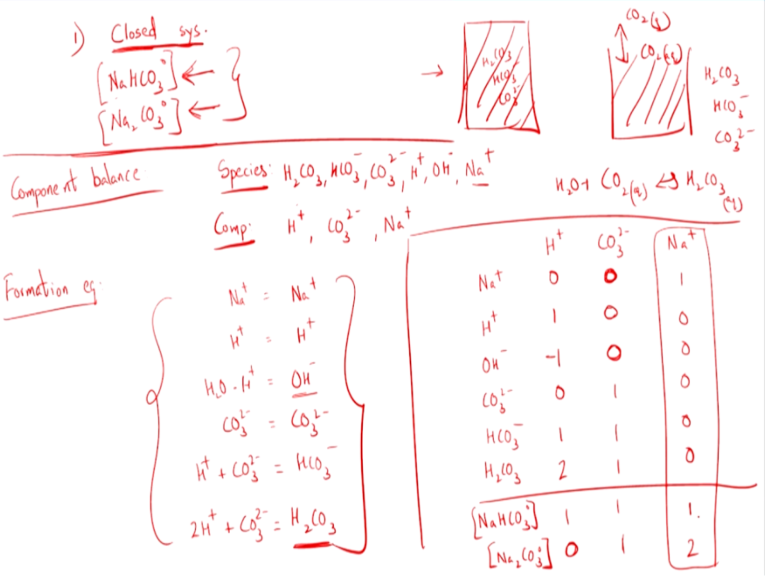

1) Closed sys.

$[NaHCO_3^0] \leftarrow$
$[Na_2CO_3^0] \leftarrow$

Component balance

Species: $H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-, Na^+$

Comp: H^+, CO_3^{2-}, Na^+

$H_2O + CO_{2(aq)} \leftrightarrow H_2CO_{3(aq)}$

Formation eq:

$Na^+ = Na^+$
$H^+ = H^+$
$H_2O - H^+ = OH^-$
$CO_3^{2-} = CO_3^{2-}$
$H^+ + CO_3^{2-} = HCO_3^-$
$2H^+ + CO_3^{2-} = H_2CO_3$

	H^+	CO_3^{2-}	Na^+
Na^+	0	0	1
H^+	1	0	0
OH^-	-1	0	0
CO_3^{2-}	0	1	0
HCO_3^-	1	1	0
H_2CO_3	2	1	0
$[NaHCO_3^0]$	1	1	1
$[Na_2CO_3^0]$	0	1	2

So let us look at that I guess the two aspect we need to clarify first 1 that we will work it for closed system and where will I working it out for specific question that arrive is where we looking at specifically a closed system and where we define that specially now right at as we just discussed in lasted few minute we see that H2CO3 right can be in equilibrium or will be equilibrium with the carbon dioxide in the gaseous phase.

So for example let us say a solutions that has carbonic acid or the carbonate system in it is open to the atmosphere let us say it is not close anymore but it is open to the atmosphere. So depending upon the relevant concentration the carbon dioxide in the atmosphere can either dissolve into the aqueous phase or the carbonic acid or reach equilibrium or leave the system as CO2 into the gaseous phase again.

So just try to represent what we are been talking about so for example let us say this is my closed system and there is a specific concentration with respect to H2CO3 HCO3 – and CO32- let us say right but later on let us say open up the system breaking the concentration are going to stay the same with respect to H2CO3 HCO3 – and CO3 2 – no and why is that because the carbonic acid is going to be in equilibrium right or the carbon dioxide is in gaseous phase is going to be in equilibrium with the carbon dioxide in the aqueous phase and what do you see here.

So you can either see a transfer of CO2 from the gaseous to aqueous or vice-verse depending upon the relevant concentration and we know that CO2 in the aqueous phase is going to be in equilibrium with H2CO3 in the aqueous phase right. So that is what we just discussed so we are going to work it out for 2 aspects right and obviously that is relevant here.

So whenever somebody talks about carbonate system let us say or in experiment involved in carbonate you need to look at you know are trying to maintain a carbonate concentration and if so you know would stay in equilibrium with the partial pressure that you would expect in your particular atmosphere or is it a closed system if so then that can go ahead right anyhow let us come back to our drawing table here.

And we are now working it out for closed system which is not open to the atmosphere right and let us say for the sake of an example let us say we are adding NAH CO3 and NA2CO3 to our system at relevant concentration let us say these are all recipes species are initial concentration that we are adding to our system. So I am adding NAAH CO3 and NAACO3 to the system and I want to know what I going to the PH and what are the relevant concentration of your various species that you would expect in this particular system.

So let us look at that again obviously what are we going to look at the only way to solve this is going to be the component balance component balance right. And whenever we look at component balance we obviously need to define the species so for this particular carbonate system we know that the species are going to be H2CO3 HCO3 – and CO32- the relevant acid and conjugate basis or acid right and what else we are always going to have H+ and OH- and here also have sodium also going to have relevant this salt here right.

And because this is a close species we do not have any other gaseous phase species such as carbon dioxide here but if where an open system would which we are going to work out in the next lecture session or once we have done with this particular aspect we are going to list we need to list carbon di oxide in the gaseous phase 2 right we are looking at species as in what is the system we are trying to analyze the system at equilibrium.

So in this particular case it is a closed system it is not open to the atmosphere then there is no chance of equilibrium with gaseous phase or no gaseous phase species in our list right and then key is to choose the components and what is the component obviously we also try to choose H+ or the proton and then the most deprotonated form of the acid and that is going to be CO3- and then the sort of the sodium here right and then the formation equation let us list them out please the formation equations.

So I am going first list all the species here so I will go with the easier one first NA+ H+ OH- CO32- HCO3- and H2CO3 right. So let us see how to form them I need component of NA+ to be able to form NA+ I need one component of H+ to able to form H+ I need -1 component of H+ to be able to form OH- and I need one component of CO23- to form CO3- I need one each of H and CO32- to be able to form HCO3- an d similarly I need two components of H and one component of CO32- to be able to form my particular H2CO3 here right.

So I am done with the formation equation here so obviously the next step would be the tableau right and first you are going to list the component they are H+ and what else CO32- and NA+ again I am going to list the species so NA+ H+ OH- CO32- HCO3- and H2CO3 right. When the tableau though we are also going to always have to list our recipe species or the species that we are adding to the system initially and these are the two species here what are they here please NAH CO3 naught are the initial concentration of NAHCO3 that you are putting in and NA2 CO3 naught.

So again we have a close system we are adding NAHCO3 and NA2CO3 initially and that is going to dissolve both this compounds are going to dissolve and then they are going to form new species which we just listed right and then here are trying to break the concentration at equilibrium right.

So again let us move on here and from the formation equation I am going to write this down it is going to be 1, 0, 0, 0, 0, 0 and 0 and it is going to be 1 component required here and two components of sodium required here right and here we have six and 6 we are done their this is going to be 0, 1, -1, 0,, 1 and 2.

And where do we get these values from obviously from your formation equations here right the if you look at the coefficients here of the relevant component here that is where we get that from and CO32- here it is going to be union of CO32- 0 components of CO32- to form NA + 0 component of CO32- to form H+ similarly with OH- that with respect to CO32- you need 1 same case with HCO3- and H2CO3.

And now coming back to your particular initial species and for CO32- so it is going to an 1 here and 1 here and here it is going to be 1 and 0 right. So we will neglect HA+ please usually place let to know for the role right it is a salt it does not play further role so we are going to only look at the total component balance with respect to PH and with respect to the CO32- right. So we will work that further and see how we can analyze the system and understand what are the relevant variables that we are going to consider in a closed system right. So let us move on let me see if an remember.

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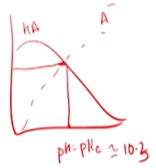
$$H_t = [H^+] - [OH^-] + \underline{[HCO_3^-]} + 2\,\underline{[H_2CO_3]} = [NaHCO_3]^0$$

$$H_t = [H^+] - \frac{K_w}{[H^+]} + \alpha_1 CO_{3t} + 2\,\alpha_0 CO_{3t}$$

$$\rightarrow \underline{H_t} = [H^+] - \frac{K_w}{[H^+]} + (\alpha_1 + 2\alpha_0) CO_{3t} = \underline{\underline{[NaHCO_3]^0}}$$

Closed:

$$\boxed{H_t,\ CO_{3t},\ pH}$$



VMINTEQ

$$[NaHCO_3]^0 = 5\ mM$$

$$[Na_2CO_3]^0 = 5\ mM$$

$$H_t = [NaHCO_3]^0 = 5\ mM$$

$$CO_{3t} = [NaHCO_3]^0 + [Na_2CO_3]^0 = 10\ mM$$

$$Na_t = [NaHCO_3]^0 + 2\,[Na_2CO_3]^0 = 15\ mM$$

So H total is going to be equal to H+- OH- and what else we have I believe we have HCO3- and we will certainly have two times H2CO3 and that is going to be equal to what now you are NAHCO3 naught so let me see if we miss anything so 1, 2, 3, 4 species are going to contain the H+ and that is going to be equal to NAHCO3 naught 1 times right and same case with CO32-.

So the CO3 total component balance is going to be equal to what now please concentration of CO32- + concentration of HCO3- + concentration of H2CO3 and that is going to be equal to NAHCO3 but you are putting initially and also to NACO3 that you are putting in initial right so let us go back and that is what we have here. So again what do we have here we are balance component with respect to H here and the only the source of the component is the initial NAHCO3 that you are putting in.

The same case we are balancing the CO3 total here in the second equation and the only source of your particular CO3 in your system is the NAHCO3 and NA2CO3 that you are plugging in initially right. So I believe here I have around 6 species but with the sodium we are able to or we can calculate the sodium concentration. So let us remove that has a unknown so we are left with 5 variables but here we have only two component balance equation thus we have only two equation here so for 5 variables we have two equations and thus we are still looking for the other three.

And obviously here we are looking at equilibrium solution right so obviously the answer lies in looking at equilibrium or the relevant equilibrium constants so let us try to write down or figure out what is the relevant equations are obviously these are acid and base systems we have the relevant dissociation equations right. So let us right them down so you know that H2CO3 can dissociate into what now H+ and HCO3 – we are going to have that and again HCO3- can further dissociate or further stay in equilibrium with H+ and CO32- right.

H2CO3 will stay in equilibrium with CO3- and CO32- and obviously we always have water dissociation right H++ OH – and so I am going to list the relevant equilibrium constants KA1 and KA2 for the 2 proton that can be released by H2CO3 and the water dissociation constant KW and KA1 is going to be equal to activity which I am going to approximate by H+. H+ into HCO3- by concentration of H2CO3 right and similarly I am going to have K2 = H+ into CO32- by concentration of HCO3- and KW is going to be equal to concentration of H+ into the concentration of OH- right.

So obviously all these need to be define in terms of activity right but we are assuming that we are ionic strength is relatively less and thus we can approximate activities by the concentration right so that is what we have here. And we have three additional equations right and so we can solve for our 5 unknowns yes.

So here we have two component balance equation right two equation from the component balance of H total and CO3 total and we have 3 total equation from the relevant acid dissociation constants right or equilibrium coefficient too and that is general so let us see how we can analyze this further but for we are going to concentrate obviously on H total I guess right. So obviously has we discussed earlier two and we looked a ionization fraction we derive using these three equations right.

So you will have alpha naught is going to be equal to what naught H2CO3 times the concentration of H2CO3 + HCO3- + concentration of CO32- right and that as you can see denominator. What is the denominator = now right and that is going to be equal to or similar to this particular variable here so it is going to be equal to CO3 total right and we are going to use that further similarly alpha1 is going to be equal to HCO3 – by CO3 total and alpha 2 is going to be equal to CO32- by CO3 total.

Again where do we have this from? CO3 total it is from this particular equation here right and anyway we are done with that now so let us try to analyze solve for this particular equation here H total so I will move on to the next slide here so H total = concentration of H+ - concentration of OH- + concentration of HCO3- +two times concentration of H2CO3 right so that is what we have here and we know that this is going to be equal to NAH CO3 that we have initially right.

And now taking it further think finite or simplifying it so that we have it only in terms of H+ I am going to have it as KW / H+ and HCO3 – what do we just have here I guess and HCO3 – we have here so thus HCO3 – is going to be equal to alpha 1 into CO3 total right so that is what we just had in the earlier slide + two times and what is H2CO3? H2CO3 we can get from this equation here that is going to be equal to alpha naught into CO3 total right.

So two times alpha naught CO3 total thus we are going to arrive at H+ - KW / concentration of H+ + alpha 1 + 2 alpha naught into CO3 total and this we have know anyway for our particular system we are initially adding NAHCO3 so that is going to be equal to NAHCO3 naught right. So again we are looking at carbonate system why because it is ubicutas because we are going to be present in most of almost engineering systems and certainly in the natural systems right and we try to analyze it for a close system when it is not open to the atmosphere and here we have relevant particular variables.

So let us look at what they are so in general the variables you need consider in your carbonate system which is closed for the close system what are the variables H total CO3 total and PH right and these in all your variables are going to depend upon these three factors and thus obviously different from your particular equation here. So we just looked at how to analyze the closed system right by hand.

And now we are going to move on to analyze the system by our particular software VMINTEQ and for this let us look at particular values with respect to the recipe species take NAHCO3 naught = 5 mili molal and let us for the sake of is NA2CO3 naught to also be 5 milli molal right. So again here we are trying to work it out by VMINTEQ and we are saying that both our recipe species or the compounds that you are putting in or adding to the solution initially which is NAHCO3 and which are NA2HCO3 and NA2CO3 are both equal to 5 milli molar ah concentration right.

So again before we plug in VMINTEQ right we always want to understand or try to predict the species or at least certainly the PH so let us try to take a call on that so keep in mind that we are adding HCO3 and I believe CO32- sources of HCO3- and CO32- and we are doing that at relatively the same concentration right.

So more or less we are adding the conjugate acid and base right so we are adding that on the same concentration the key is that we are adding them at same concentration so thus what would you expect that the PKA would be equal to the PH right as we know from the protonated form and deprotonated form or at equal concentration when is that? That is only going to the concentration when PH = PKA and I think that PKA where around or 10.2, 1.3 so let us see where we are going to be right.

So first we need to define our H total and that I believe = NAHCO3 naught right and that is going to be equal to 5 milli molal and what is CO3 total that is going to be equal to NAHCO3 naught + NA2 CO3 naught and that is going to be equal to 10 milli molal and sodium is sodium is going to be equal to NAHCO3 naught + two times NA2 CO3 naught so that is going to be equal to 15 milli molal right.

So 5, 10 and 15 so let us plug this in into VMINTEQ and here we have PH to be calculate from mass balance ionic strength to be calculated so I use the units as mili molal and first we are going add H+ or I guess initial we have C here so we going to add CO32 – and we believe we had that to be 10 milli molal concentration right so we will have that at 10 and add that to the list and next app should be H and that we said was going to be equal to 5 milli molal so that is going to be 5 milli molal and we have sodium and that we said is going to be = 15 milli molal and that going to be add to the list.

So let me check or confirm that all the three or the relevant concentration that we want so the three component where H at 5 milli molar CO3 at 10 and NA total at 50 right so we are on the right track and I am going to go back to main menu and run a MINTEQ and so obviously the PH is now nearer to the PKA value of 10.2 or 10.3.

So that is something we are find with and we see that we have different concentration here right and 1 reason why the PH might be slightly off is that the ionic strength is relatively high so that is going to affect your particular concentration and that is what you see here I guess 4.2 here and 2.4 here and so on and more importantly let us look at the species distribution that will give an idea about will tell you in what forms or in what percentage is CO3 total or CO3 has not has.

So it looks like it present as we know CO32- HCO3- right and looks like nothing will be present at H2CO3 why is that because PH is 10.7 so looks like 42% is present as CO32- right and 51% is present as HCO3 – and 1 particular species that we missed was NAC3 I believe that KA value for or the equilibrium concentration would be relatively less or negligible but that seems to be a minor error their or minor assumption that should not be taken.

So anyhow VMINTEQ confirms this so that we have 42% as CO3- and 51% as HOC3- and why do have slightly higher concentration of HCO3- compare to CO3 2- that is because the PH is 10.07 and PH is 10.07 and PKA is 10.3 so right which one will permanent now the protonated form will predominate and protonate form in this case for that PKA2 is HCO3-.

So HCO3- is slightly higher concentration right and then compare the CO3- concentration and I believe that is what we are going to see here HCO3- is slightly higher than CO32- right I guess with that we will done with today lecture session. So in the next lecture session or couple of lecture sessions anyway we are going to analyze the open system right and with that I will end my session for today and thank you.